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PRODUCTION OF FACING TILES FROM LOW-QUALITY CLAY INITIAL MATERIALS

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It is shown that ceramic facing tiles with satisfactory characteristics can be obtained from low-quality polymineral clays by semi-dry pressing. The following special methods must be used to improve the quality of the clay initial materials: process the initial material in electro-mass-classifier, mix clays with activated water, and introduce technological additives (mechanically activated quartz-glauconitic sands, refractory clay) into the initial material. Lime clays and zeolite-bearing siliceous rock can be used to expand the raw materials base for tile production.

High-quality fire-resistant and high-melting clays are required to produce ceramic tiles. However, the reserves of such clays in Russia are limited and new, unconventional types of raw materials must be brought into the production process. The problem of producing a competitive product can also be solved by increasing the quality of the natural clays, using effective processing methods for this purpose.

Unconventional technological additives and the activation of raw materials in an electro-mass-classifier can be used to improve the properties of polymineral clays to be used for manufacturing articles with the required characteristics.

Polymineral Quaternary clays which according to their properties belong to different mineral-technological varieties — 3a (montmorillonite content 35%) and 4a (montmorillonite content 28%) — were investigated [1].

The tiles were made by pressing under 25 MPa pressure molding powder with moisture content 7 – 10%. Sintering was conducted at 1000 – 1100°C (the rise rate of the temperature was 100°C/10 min) with soaking for 15 min at the final temperature.

Samples of the initial type-3a clay did not meet the requirements set by the standards. Good results were obtained by using clay which was pre-processed in an electro-mass-classifier [2]. In such processing, the clay is activated by an increase of the active surface as a result of breaking of numerous bonds during the dispersing and disaggregation of the clay particles. The granulometric composition of the clay also changes. A highly disperse molding powder where more than half (65%) the particles are smaller than 63 ìm was obtained. The tiles obtained from such molding powder possess bending strength 17 MPa and water absorption 7.8%. This attests to the fact that the activation performed increases the activity of the clay particles and improves the sinterability of the powder, i.e., it permits converting this clay raw material into a conditioned material.

Processing a mix consisting of 80%[2] initial clay material and 20% high-melting clay in a electro-mass-classifier increases the bending strength of the samples even more (up to 22.1 MPa) while increasing water absorption by a small amount (8.1%). The increase of water absorption could be due to the change of the structure of the pore space as a result of the change of the granulometric composition of the molding powder.

The photoluminescence method established that additional luminescence lines associated with Mn^{2+}, Fe^{3+}, and Al^{3+} ions appear in the spectra of the activated clay. The band intensities of the spectra change by 20 – 22%. The electron paramagnetic resonance spectra of the initial sample and a sample which completed the electro-mass-classifier cycle differ by a shift of some regions of the spectrum into regions where the *g* factors are large (from 3.0 to 3.5) and by the appearance of new lines and increase (by up 10%) of the intensity of the overall spectrum from the Fe^{3+} ions. The result can be explained by the oxidation of iron from divalent to trivalent.

Mechanically pre-activated quartz-glauconite sands are quite effective technological additives. Their introduction into the ceramic mix in the amount 20% made it possible to obtain samples with bending strength 20 MPa, water absorp-

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[2] Here and below — content by weight.

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TABLE 1.

Sample	Mix composition, %						$CaCO_3$ content in limy clay, %
	limy clay	high-melting clay	cullet	chamotte	quartz sand	nepheline concentrate	
1	82	–	–	–	–	18	13.7
2	90	–	10	–	–	–	18.7
3	70	20	–	5	5	–	24.5
4	80*	–	15	5	–	–	14.0
5	85	–	–	5	10	–	13.8

* Mixture of two assays in ratio 1 : 1.

tion 6.5%, and fire shrinkage 3%. In this case the samples also satisfy the standard requirements for these parameters.

Expanded technological tests performed on optimal ceramics mixes showed that the glazed facing tiles obtained for interior and exterior work meet the requirements of the normative-technological documentation with respect to all regulated parameters.

Likewise, the characteristics of the samples prepared from the type-4a initial clay by the slip technology are unsatisfactory. Processing this clay in an electro-mass-classifier gives only a slight improvement of the properties of the tiles (the bending strength increased by 12%, the water absorption decreased by 0.4%). The indicators for the samples obtained from slip to which high-melting clay was added in the amount 20% are good (bending strength 17.6 MPa, water absorption 10.4%, total shrinkage 1.6%). Using activated water to prepare the slip is also effective.

The dominant trend in the production of ceramic facing articles is wide adoption of more readily available and therefore less expensive argillaceous rocks which contain no or only a small amount of kaolinite. Limy clays in which the carbonate component is uniformly distributed should be included among these raw materials.

The use of limy clays for manufacturing light-colored tiles is promising and economically profitable. Together with the expansion of the raw materials base, there is also the important fact that glaze deposited on a light-colored substrate is thinner while at the same time there is no loss of color. In addition, silicon and calcium oxides are present simultaneously in such rocks, and the interaction of these compounds during roasting results in the formation of wollastonite, which improves the application properties of articles.

Electron-microscopic investigations have shown that the clay-carbonate component of the rock from the Maksimkovskoe deposit in the Republic of Tatarstan is uniformly granular, the average size of the concretions of the argillaceous minerals and grains of organogenic calcite is 3 – 5 μm. In limy clays, the temperature at which the calcite begins to break down is anomalously low; this is explained by the organogenic nature of calcite.

The mineral composition of limy clays is: 35 – 80% agrillaceous minerals, 10 – 55% calcite, and 1 – 5% quartz. The average content of calcite is 30%. Gypsum, pyrite, glauconite, and iron hydroxides are present as impurities.

X-ray phase analysis established that as a result of the high-temperature treatment wollastonite $Ca_3Si_3O_9$ and gehlenite $Ca_2Al[(Si, Al)_2O_7]$ form, by solid-phase synthesis, from a mixture of argillaceous minerals and calcite which contains the cations Ca^{2+}, Si^{4+}, Al^{3+}, and Fe^{3+}. Iron is present in two main phases in the products of roasting of limy clays with $CaCO_3$ content from 15 to 30% — wollastonite, where the Fe^{3+} ions isomorphically replace Ca^{2+} in the octahedral positions, and hematite, where the Fe^{3+} ions are the structure-forming elements. For calcite concentration 50%, iron is in the form of hematite and gehlenite; isomorphism $Fe^{3+} \to Al^{3+}$ is observed in eight-fold and tetrahedral coordinations. An elevated content of the carbonate component in the initial argillaceous rocks allows the calcium-containing silicates to become predominant in the composition of the ceramic during roasting.

The optimal composition of the mix based on limy clay was determined. It yields ceramic facing tiles with acceptable physical – mechanical properties (bending strength — at least 15 MPa, water absorption — no more than 24%) and external appearance. It was determined that to prepare such a mix it is best to mix in definite proportions rocks with different contents of carbonates with the addition of high-melting plastic clay (20%), nepheline concentrate (18%), cullet (10 – 15%), chamotte (5%), quartz sand (5 – 10%), and other adjusting additives in order to attain the control indicators: $CaCO_3$ — 28 ± 3%, $Al_2O_3 : RO \sim 1$, $Al_2O_3 : R_2O \sim 4 – 7$.

An initial mix with a prescribed content of carbonate and adjusting additives, which when roasted forms a light-colored ceramic material with satisfactory physical – mechanical properties, can be obtained from different varieties of limy clays by mixing weighed portions.

Experimental batches of light-colored, large, facing tiles for use in interior work which meet the standard requirements (bending strength 15.4 – 22.0 MPa, water absorption 13.8 – 21.7% (Tables 1 and 2)) were obtained. Various additives make it possible to obtain samples with the required pa-

TABLE 2.

Sample	Water absorption, %	Bending strength, MPa	Total shrinkage, %
1	19.7	16.2	2.4
2	14.0	21.9	3.4
3	21.7	15.4	2.5
4	17.6	17.8	3.9
5	13.8	22.9	4.0

rameters from clay initial material with carbonate content 20 – 40%. Roasting is best performed in a furnace with a temperature gradient of no more than 10°C over the cross section of the roasting channel.

It was established that it is possible in principle to deposit a layer of glaze on the light-colored ceramic surface of the tiles. For this, majolica glazes from the Dulevo Color Works were used. However, from some glazes it was impossible to obtain a high-quality coating (pinholes were present). This is due to the elevated gas production due to the interaction of the glaze with the ceramic. This process is most noticeable on the surface of samples made from initial materials with an elevated carbonate content (> 25%).

Most glazes used in commercial enterprises for glazing tiles manufactured from non-limy initial materials can be used, without adjustment, for coating articles manufactured from limy clays. For this, it is necessary to find glazes whose composition precludes their chemical interaction with the ceramic base and makes it possible to obtain an even and lustrous coating.

The possibility of obtaining light-colored ceramic tiles from zeolite-bearing silicon rock (ZBSR) from the Tatarsko-Shatrashanskoe and Gorodishchenskoe deposits (Tatarstan) was studied. Among the main mineral constituents in these rocks, an opal-cristobalite phase always predominates; its average content is 27 – 28%, which is followed by calcite (21%), clinoptilolite-heulandite (18%), and a clay component (17.5%).

Of the mineral phases listed above, either all main components, i.e., the opal-cristobalite phase, zeolites, argillaceous minerals, and calcite, or their combinations are of commercial value depending on the applications of ZBSR. The presence of an opal-cristobalite phase and zeolite is mandatory.

Oxides of silicon (44 – 80%, usually 60 – 65%), aluminum (4 – 13%), calcium (8 – 18%), and iron (1.5 – 4.3%) play the main role in the chemical composition of ZBSR. The content of magnesium, sodium, and potassium oxides is low — 0.7, 0.4, and 2.6%, respectively. Active or free silica is always present in amount 12 – 42%, reflecting the presence of an opal-cristobalite phase.

Tiles were pressed under pressure 20 MPa from molding powder with particle size smaller than 0.5 mm. The samples were roasted at 1150°C. The color of the samples changes from gray to gray-yellow after roasting. The bending strength is 12.0 – 23.1 MPa, water absorption is 4.8 – 18.1%, and total shrinkage is 10.3 – 19.0%. X-ray structure analysis of the roasted samples showed the presence in them of low-temperature cristobalite and tridimite as well as quartz and wollastonite.

A batch of large-size tiles whose properties satisfy the requirements which interior facing tiles must meet was fabricated from ZBSR.

The investigations performed showed that it is possible to obtain from low-quality polymineral clays glazed ceramic facing tiles with satisfactory properties for exterior and interior use. For this, it is necessary to use effective methods for processing the raw materials (electro-mass-classification, mixing of the clays with activated water) and local technogenic additives (for example, mechanically activated quartz-glauconitic sands).

The raw materials base can be expanded by using limy clays and zeolite-bearing siliceous rock.

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